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WITNESS my hand this
Sixteenth day of December 2004

A handwritten signature in dark ink, appearing to be 'L. Mynott'.

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Commonwealth Scientific and Industrial Research Organisation

A U S T R A L I A

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PROVISIONAL SPECIFICATION

for the invention entitled:

"Hybrid Inorganic Polymer Systems"

The invention is described in the following statement:

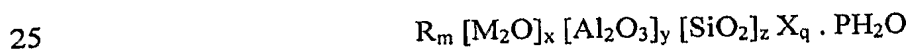
HYBRID INORGANIC POLYMER SYSTEMS

The present invention relates to Hybrid Inorganic Polymer Systems (HIPS), and more particularly to inorganic polymers that have been modified by the incorporation within their structure of organic functional groups. The present invention also relates to a process for the preparation of such modified polymers as well as their use.

The term "inorganic polymer" is used herein to denote a class of inorganic materials derived from the polycondensation of aluminosilicates and alkaline solutions. The inorganic polymers include Si-O-Al bonds and may be classified depending upon the three dimensional silico-aluminate structures generated. They are typically used as binders, for example as cements.

These types of inorganic polymers exhibit characteristic properties and it would be desirable to manipulate these properties with specific end uses in mind. For instance, it would be useful to tailor such properties as toughness, elasticity, Young's modulus, adhesion, water-resistance, surface hardness/impact resistance and thermal and flame resistance. The present invention seeks to influence and control the physical and/or chemical properties of inorganic polymers by incorporation within the polymer structure of one or more types of organic functional groups.

Accordingly, in one embodiment the present invention provides an inorganic polymer which comprises one or more organic functional group and which has the following empirical formula:



in which:

R represents an organic functional group;

M is an alkali metal, such as sodium, potassium or lithium;

X is selected from chlorine and fluorine;

m > 0;

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- q is > 0.2 ;
- x is from 1 to 1.6;
- y is from 1.0;
- x/y is from 1.0 to 1.6;
- 5 z is from 3 to 65;
- z/y is ≥ 1.0 ; and
- P is from 3 to 5.

Preferably, and independently, x is from 1.2 to 1.5 , z is from 3 to 10 and P is from 3.5 to
10 5.0.

The symbol m represents the total number of moles of organic functional group(s), R, present in the inorganic polymer of the invention. These groups R may be the same or different.

15

Conventional inorganic polymers consist of chains or networks of oxygen-linked silicon atoms, with other metals (typically aluminium), replacing silicon at regular intervals within the bulk chemical structure. In the polymers of the present invention, depending on its chemistry, the organic functional group(s) R may terminate an alumino-silicate polymer
20 chain and/or may be provided as a spacer moiety between alumino-silicate polymer chains within a network of such chains.

The polymers of the present invention are formulated with the intention of exploiting beneficial properties of both organic and inorganic polymer systems. A number of
25 different classes of hybrid inorganic polymer system may be prepared depending upon the nature of the organic functional group(s) which is/are incorporated within the structure of the polymer. The type and concentration of organic functional group introduced has been found to influence the properties of the resultant organic/inorganic hybrid polymer. In turn this enables the properties of the polymer to be tailored to a targeted functionality. It will
30 be appreciated that the inorganic polymer may be modified by incorporation of the same or different organic functional group. Incorporation of different organic functional groups

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enables the preparation of inorganic polymers which exhibit a combination of desirable properties based on the individual types of organic functional groups (and relative proportions thereof) incorporated. This can allow more precise tailoring of the properties of the inorganic polymers of the present invention.

5

The exact mechanism by which the organic functional group is bound within the structure of the inorganic polymer is unclear but this is believed to be due to ionic, covalent, hydrogen bonding or Van der Waals interactions, or a combination of two or more of these, depending upon the nature of the organic functional group.

10

Examples of modifying reagents which may be used to introduce the organic functional group include:

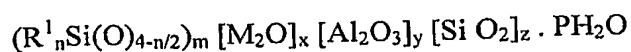
1. Organic silicon-containing compounds such as silanes, silicones and polysiloxanes.

15 Where silanes are used the modified inorganic polymer will typically have the empirical formula:



in which R^1 is an organic functional group, n is 1, 2 or 3 and the various other symbols are as defined above. Examples of organic functional groups R^1 include but not limited to
20 alkyl (in particular C_{1-4} alkyl such as ethyl, methyl, propyl and butyl), alkenyl (in particular C_{2-4} alkenyl such as vinyl, 1-propenyl, 2-propenyl and butenyl), alkynyl (in particular C_{2-4} alkynyl such as acetylenyl and propargyl), aryl (in particular C_{6-10} aryl such as phenyl and naphthyl) and the corresponding alkaryl and arylalkyl groups. The above referenced alkyl, alkenyl and alkynyl groups include the corresponding cyclic radicals such as cyclopropyl,
25 cyclopentyl and cyclohexyl.

Where silicones and polysiloxanes are used the modified inorganic polymer will typically have the empirical formula:



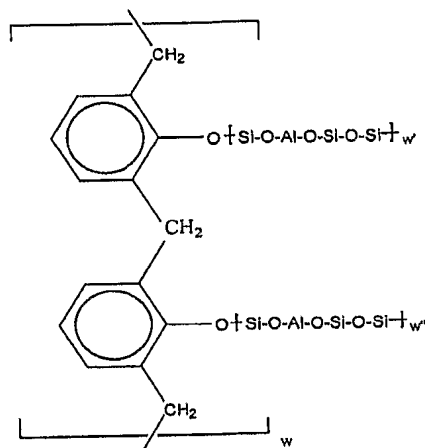
in which R^1 , m, n, x, y, z and P are as defined above. Specific examples of modifying silicone reagents include polydimethyl siloxanes (PDMS) and polydimethoxysilanes ethoxylated dihydroxyl terminated.

- 5 2. Compounds containing specific organic functional groups. As modifying agent it is possible to use compounds which will contribute specific types of organic functional groups to the inorganic polymer. In this embodiment useful compounds tend to include polar functional groups which enable the compound to be incorporated within, and thereby modify, the inorganic polymer structure. Such polar organic compounds may include
- 10 groups which are capable of forming covalent and/or ionic and/or secondary bonds during formation of the modified inorganic polymer of the present invention. Specific examples or such functional groups include phenolic, amino, amido (and polyamido), imido (and polyimido), epoxy and (meth)acrylic functional groups. These groups are believed to be incorporated into the inorganic polymer structure as spacers and/or interconnectors
- 15 between aluminosilicate chains linked primarily by having secondary bonds. Specific examples of such compounds include phenolic resins such as novolak and resole resins, polyamides such as nylon-6 and nylon-66, polyimides such as acetylene-terminated isoimide resins and benzocyclobutene resins, epoxies such as epichlorohydrin and bisphenol-A derived resins, epoxy cresol-novolak resins (ECN), bisphenol F resin and
- 20 cycloaliphatic epoxy resins, and (meth)acrylates such as poly(methyl methacrylate) and poly(ethyl methacrylate). Preferably, the compound is a phenolic compound.

If the organic functional group includes repeat units each of which is capable of forming a bond with an aluminosilicate chain, networks of crosslinked chains may result. This is

25 illustrated schematically below where the modifying reagent includes phenolic repeat units:

- 5 -



in which w, w' and w'' represent the number of repeat units.

- Depending upon its identity the incorporation of organic functional groups in accordance with the present invention has been found to influence such properties as toughness, Young's modulus, elasticity, adhesion, water resistance and processability. This means that the modified inorganic polymers may be used as a coating, binder and adhesive and in applications relying on hydrophobic/hydrophilic properties.
- As might be expected, the nature of the organic functional group within the inorganic polymer will have an influence on its specific properties, and thus on its possible end uses. For instance, it has been found that modification of the resultant inorganic polymer with a siloxane compound can enhance the elasticity and toughness of the inorganic polymer. Inorganic polymers modified in this way would be particularly useful for use as waterproofing and/or fire resistant adhesives and coatings on a variety of substrates, such as metallic and cellulosic materials. It has also been found that modification of an inorganic polymer by incorporation of a phenolic compound can lead to enhanced adhesive properties in the resultant product. Such modified inorganic polymers may be used as adhesives and binders for the production of composite materials (the polymer being used as a matrix material).

When fully formulated for use, the modified inorganic polymer of the present invention may include a variety of additives to impart particular characteristics. Thus, the polymer may include such additives as fillers, pigments, dyes, thixotropic and rheology modifying agents and reinforcing particles, synthetic and natural fibres and fillers, such as metal
5 oxides, e.g. Y_2O_3 , TiO_2 , ZrO_2 , CeO_2 , SnO_2 , ZnO , Al_2O_3 , and iron oxides, carbon (fibre, flake or particles), carbides, nitrides, borides, metal powders, polymeric materials and glass such as borate glasses. Useful fillers also include silicon dioxide type fillers, and these may assist in forming a hardened product when the modified inorganic polymer is subsequently used. Particulate and fibre reinforcement may have the same result. The
10 incorporation of additional components may enhance the mechanical properties of the inorganic polymer and/or impart specific properties such as electrical conductivity or resistance, magnetic properties and optical properties. One skilled in the art will be familiar with which additives to use and the effects they impart.

15 Polymeric compounds such as polyurethanes, styrene butadiene/nitrile rubbers and poly(vinyl chloride) may also be blended with the inorganic polymer. These polymeric compounds do not tend to be incorporated within the structure of the inorganic polymer itself in the same way as the modifying reagents described. Rather, when used, the polymeric compounds tend to act as a matrix material between the polymer chains of the
20 inorganic polymer. This in itself can lead to enhanced properties, such as flexibility, due to the presence of the polymeric compound at inter-chain locations. Obviously, the proportion of polymeric compound blended with the inorganic polymer will be influential in this respect and one skilled in the art would have no difficulty in ascertaining a suitable proportion based on the properties desired of the blended product.

25 The inorganic polymers of the present invention may be prepared by the co-condensation of an aluminosilicate, alkali polysilicate and the modifying reagent. The physical form of the modifying organic reagent may determine the way in which this co-condensation is performed. Thus, when the modifying organic reagent is a liquid, in a first step, the solid
30 aluminosilicate species are dissolved in alkali polysilicate to generate colloidal aluminate and silicate species. The modifying reagent is then added with continued mixing and the

mixture cured (typically to a temperature from 80 to 160°C) to initiate the co-condensation reaction. However, when the modifying organic reagent is a solid, the modifying organic reagent and aluminosilicate tend to be added to and dissolved in the alkali polysilicate prior to curing (typically at from 80 to 160°C) to initiate co-condensation. This technique
 5 may also be used if the modifying organic reagent is a liquid. Any additional components, as described above, are blended with the mixture prior to curing. Co-condensation leads to formation of an aluminosilicate network incorporating organic functional groups derived from the modifying reagent. Preparation of the modified inorganic polymer may be carried out using equipment conventionally used in the preparation of inorganic polymers.

10

In one embodiment curing takes place in more than one step. Here an initial curing step at relatively low temperature is employed to drive off any water present in the co-condensation mixture. Water present in the mixture prior to co-condensation can present processing problems such as delamination effects in the final cured product. The initial
 15 curing step takes place at a temperature of from 85 to 140°C. Subsequently, when water present has been removed, a subsequent final cure (typically from 80°C upto about 180°C) is effected. This multi-stage curing is usually employed when the organic compound incorporated into the inorganic polymer system is or includes a phenolic functional group.

20 Typically, the composition $\{R_m[M_2O]_x[Al_2O_3]_y[SiO_2]_zX_q.PH_2O\}$ of the reactant mixture in terms of mole ratios falls within the ranges given in the following table.

Compounds	$[M_2O]_x$ (M=Na, K)	$[Al_2O_3]_y$	$[SiO_2]_z$	X_q (X=Cl, F)	R	
					Organic silicon- containing compound	Other organic compound
Molar ratio	1.0~1.6	1.0	3.0~65.0	0.2-20.0	-	
Percentage (%)	80 ~99.9				20~0.1	-
	10~99				-	90 ~ 1
	10~99				5-0.1	85 ~ 1

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The feedstocks for the reaction are commercially available or may be made by the application or adaptation of known techniques. As a source of aluminosilicate naturally occurring or synthetic solid silica-rich aluminosilicates may be used. Examples include calcined clays and fly ash produced from coal-fired power stations. Alternatively, the aluminosilicate may be prepared from a polyhydroxy-alumino-silicate according to conventional techniques. Useful modifying reagents are commercially available or may be made by the application or adaptation of known techniques.

The product of the co-condensation reaction is typically a resinous material having enhanced properties compared to conventional (unmodified) inorganic polymer systems. The introduction of organic functional groups into the polymer structure enables the properties of the end product to be tailored to the intended application of the polymer. The properties of the modified inorganic polymers tend to be a combination of those pure inorganic and organic materials.

The modified inorganic polymers of the present invention may be used in a variety of applications depending upon their properties, as described above. Broadly speaking, the HIPS of the invention may be used as an adhesive or coating, or as a binder in manufacturing and processing technology.

In adhesive and coating applications the HIPS resin product is applied to the surface of one or more substrates and cured by elevated temperature or a combination of pressure and elevated temperature. In the construction industry the HIPS may be used to produce laminates and plywoods, and to bond a variety of materials together. The HIPS may be used on, for example, timber, timber-based products and metals (e.g. steel). In the electrical/electronics industry the HIPS may be used to manufacture circuit boards and electronic components, such as semiconductors. The use of the HIPS to manufacture circuit boards (under high pressure and temperature) results in a rigid product having good electrical, temperature and corrosion resistance, and good dimensional stability. The HIPS may therefore be used in place of conventional materials such as epoxies, polyesters, melamine, phenolics, polyimides and Teflon. The resin may be applied using conventional

tools and methods as for organic resins eg epoxy, but cured at temperatures of 80°C to 120°C. It has been found that manipulation of the relative proportions of organic and inorganic constituents enables the properties of the resultant HIPS to be controlled. For example, it may be possible to control the thermal, chemical and/or water resistance as well as mechanical, electrical and/or adhesive properties.

When used as a binder the HIPS is blended with a functional additive, which may be a powder, granule or fibrous material, shaped and then cured by the action of heat, or a combination of heat and pressure, to form a monolithic product. During curing co-
 10 condensation reactions result in formation of a thermally stable composite product. The nature of the functional additive and the proportion included in the composite will dictate the end use of the composite. Typical uses of such composites include automotive and aviation products such as brake and clutch components, engine moulds, tyres and lining materials (such as vehicle cockpit linings, parcel shelves etc). Such linings typically use
 15 paper or natural or synthetic materials (e.g. cotton, glass) in fibre or yarn form, as the additive. The HIPS may also be used to form foundry moulds for high temperature casting applications. For instance, the kind of HIPS described in Example 2 below may be used as a binder to form a foundry mould. Here the HIPS is blended with a suitable refractory material such as sand and, optionally, additional foundry additives. The HIPS is then
 20 moulded to the desired configuration and cured (a multi-stage cure is likely to be employed).

Phenolic-based HIPS in accordance with the invention are also particularly well suited to manufacture of automotive and aviation components such as brake pads and clutch linings.
 25 Here the HIPS resin is used as a binder material and blended with appropriate functional additives. Usually an initial low temperature cure is employed to drive off water followed by a final cure at a temperature of between 80 and 170°C. Alternatively, a single hot press forming and curing operation may be employed.

30 The following non-limiting examples illustrate the present invention:

Example 1: HIPS synthesized with poly(dimethylsiloxane ethoxylated dihydroxyl terminated):

In Method 1, a suspension of colloidal powders, was prepared from 60g metakaolin, 102g
5 sodium silicate solution (ratio of Na_2O to $\text{SiO}_2 = 1:2$) and 10g of poly(dimethylsiloxane
ethoxylated dihydroxyl terminated) to produce a suspension of colloidal powders. Intimate
mixing by stirring of suspension may enhance association of organic and inorganic
components at the molecular level. The HIPS slurry was cast into cubic shape, and cured at
85°C. The resulting samples showed good compressive strength and water resistance.

10

Example 2: HIPS synthesized with phenolic resin:

A HIPS was prepared from metakaolin and alkaline silicate solutions as in Example 1 but
with phenolic resin (aqueous phenol formaldehyde having a specific gravity of 1.2 at
15 25°C) being used as the modifying reagent. The HIPS formulation was synthesised by
adding 40g phenolic resin to 60g base inorganic formulation and mixing the slurry by
stirring i.e. @150°C. The physical characteristics of the resulting gel network depend
greatly on the size of particles and extent of cross-linking prior to gelation. The HIPS
slurry was applied as an adhesive and cured at 150°C for 120mins. The cured HIPS
20 showed strong bonding force at both room and high temperatures.

Dated this 2nd day of December 2003

Commonwealth Scientific and Industrial Research Organisation

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